

Oxidation States of Manganese in Soil Minerals

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Introduction: Manganese is a plant essential micronutrient required for a number of critical biochemical processes, most importantly photosynthesis. Mn uptake is determined by oxidation state and we are particularly interested in understanding the spatial and temporal distributions of Mn in the rhizosphere, the region of soil that is strongly influenced by root exudates and inhabited by soil borne, plant pathogenic fungi (e.g. *Gauemannomyces graminis*) that appear to oxidize Mn during disease initiation. MicroXANES is excellent for measuring Mn oxidation state at high spatial resolution in the vicinity of live roots but since XANES measures all Mn within the volume traversed by the primary beam, a full understanding of Mn oxidation state in all Mn-containing minerals is necessary. The most chemically reactive Mn in soils occurs as highly reactive colloidal particles. Once the highly reactive Mn has been extracted from the soil, the remaining Mn occurs as Mn^{II} and Mn^{III} , apparently in primary minerals in the sand and silt size fractions, and in phyllosilicate minerals in the clay fraction. This past year, we have used microXANES spectroscopy to study Mn oxidation states in soil minerals in the fine and coarse clay fractions, and in individual sand grains.

Methods and Materials: A soil from West Point, Indiana (Typic Argiudoll), was exhaustively extracted with dithionite-citrate-bicarbonate (DCB) to remove all of the reactive Mn oxides, then fractionated into different particle size fractions. XANES spectra of the fine and coarse clay were obtained on bulk samples. The 125-250 μm sand fraction was embedded in ScotchcastTM resin, a 30 μm thin section as prepared, and individual grains were analyzed by microXANES. X-ray diffraction was used to identify the mineralogy of the clay fractions, and optical microscopy and electron probe microanalysis were used to identify the minerals in the sand grains.

Results: Most of the Mn remaining after DCB extraction is found in the clay fraction. Smectite, mica, and kaolinite are the main clay minerals in the clay fractions, and the XANES spectra of the clay fractions match those obtained for the bulk soil after exhaustive DCB extraction (Fig. 1). The individual sand grains show more variability in their XANES spectra (Fig. 2). Quartz and feldspar, which contain very little Mn, give very poor XANES spectra, though what Mn they do contain appears to be primarily Mn^{II} and Mn^{III} . The Mn XANES spectra for the biotite and ilmenite grains show prominent features below the edge energy for aqueous Mn^{II} , indicating that while the Mn oxidation state is probably +2, the XANES edge structure is influenced by the coordination environment of the Mn. A grain tentatively identified as weathered feldspar has a XANES spectrum with a very prominent Mn^{II} peak, and an opaque grain had an identical XANES spectrum (data not shown). Even in these primary mineral grains, Mn is associated with Fe. Grains that contain elevated levels of Mn also contain elevated levels of Fe, though the opposite is not always true (data not shown).

Conclusions: Mn in primary soil minerals appears to contain Mn^{II} and Mn^{III} . In general, Mn is associated with Fe, possibly substituting for Fe^{II} and Fe^{III} in octahedral coordination in the mineral structures. In some cases, the XANES edge structure is strongly influenced by Mn coordination environment, in addition to Mn oxidation state.

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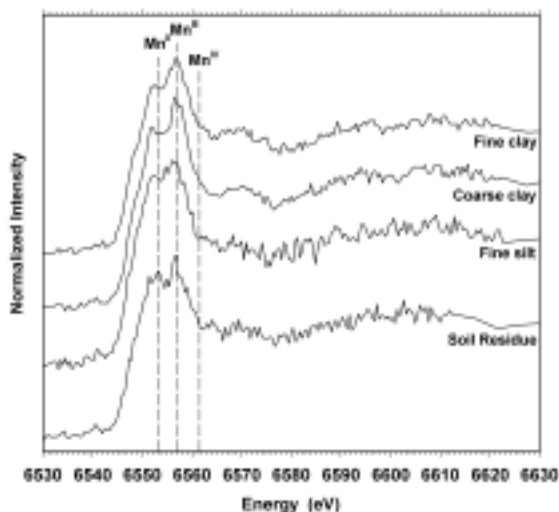


Figure 1. Mn XANES of fine clay, coarse clay, and fine silt fractions after DCB extraction.

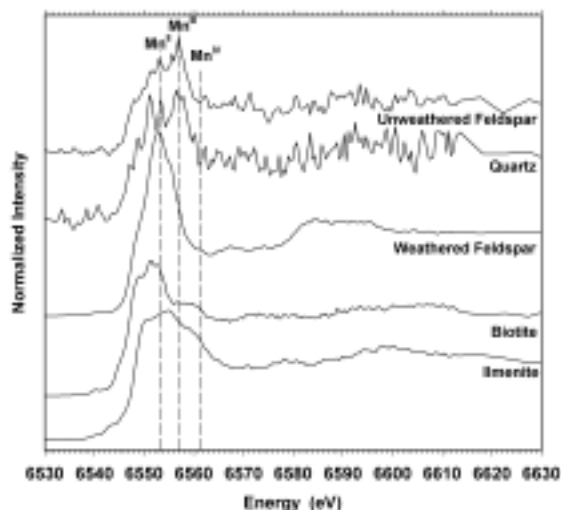


Figure 2. Mn XANES of individual mineral grains from the 125-250 μm sand fraction.